

Direct Entropy Determination and Application to Artificial Spin Ice

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From thermodynamic origins, the concept of entropy has expanded to a range of statistical measures of uncertainty, which may still be thermodynamically significant[1, 2]. But, laboratory measurements of entropy continue to rely on direct measurements of heat. New technologies that can map out myriads of microscopic degrees of freedom suggest direct determination of configurational entropy by “counting” in systems where it is thermodynamically inaccessible, such as granular[3–8] and colloidal[9–13] materials, proteins[14] and lithographically fabricated nanoscale arrays. Here, we demonstrate a conditional probability technique to calculate entropy densities of translation-invariant states on lattices using limited configuration data on small clusters, and apply it to arrays of interacting nanoscale magnetic islands (“artificial spin-ice”[15]). Models for statistically disordered systems can be assessed by applying the method to relative entropy densities. For artificial spin-ice, this analysis shows that nearest neighbor correlations drive longer-range ones.

Our artificial spin ice[15] systems are arrays of lithographically defined single-domain ferromagnetic islands (25 nm thick and 220 nm × 80 nm in area) on the links of square and honeycomb lattices (Fig. 1). Shape anisotropy forces island moments to point along the long axes, forming effective Ising spins. The coercive field is about 770 Oe (i.e., a barrier of order 10⁵ K), while the field from one island on a neighbor only of order 10 Oe (10⁴ K). The arrays are demagnetized by rotating in an in-plane external magnetic field H_{ext} , initially strong enough to produce complete polarization, subsequently reduced to zero in small increments[15, 16] ΔH_{ext} , with reversal of the field at each step. For small step sizes, the result is a statistically reproducible macrostate, operationally defined by the demagnetization protocol[15, 16], which is probed by magnetic force microscopy to obtain the static moments of individual islands. We want the entropy of a single macrostate, but distinct runs might produce distinct macrostates (for example, a residual magnetization at larger step size). In most cases, data are

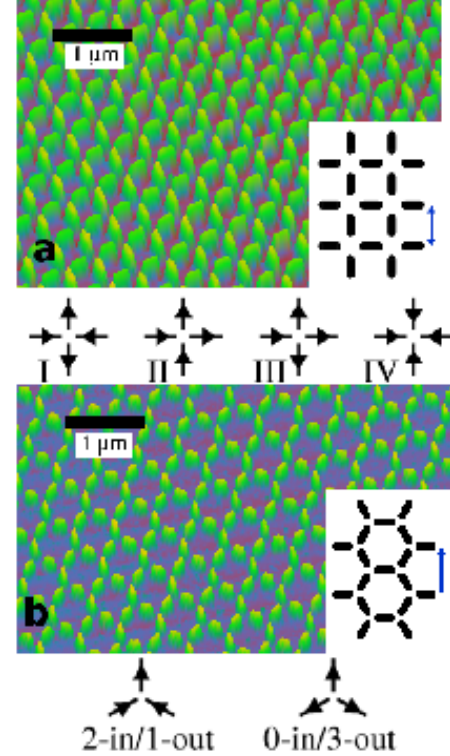


FIG. 1. **Artificial spin-ice arrays.** **a.** AFM image of 400 nm square lattice with inset showing lattice spacing, and schematics of vertex types. **b.** Similarly for 520 nm honeycomb lattice.

collected in a single run, averting the problem, but the entropy of macrostate mixture would be relatively unimportant anyway, as is shown in Supplementary Information §3. For large structurally regular systems such as ours, it is more appropriate to work not with total entropy, but with entropy density [See Eq. (2)] having units of bits/island, a value of 1 corresponding to complete disorder.

The strongest interactions, between islands meeting at a vertex, favor head-to-tail moment alignment. But not all these can be satisfied simultaneously, resulting in a kind of frustration. Still, for the square lattice,

the ground state is only two-fold degenerate[15], since Type-I vertices, as defined in Fig. 1, are lowest in energy. That the ordered ground state is never found experimentally[16, 17] suggests that the evolution is kinetically constrained[18, 19]. For instance, one spin flip converts a Type-II to a Type-III; flips of two perpendicular islands are required to reach Type-I. In contrast to the square lattice, the honeycomb lattice has a macroscopically degenerate ground state when only nearest or next-nearest neighbor interactions are effective (longer-range interactions break the degeneracy[20] at a much lower energy scale). The interactions prefer a 2-in/1-out or 1-in/2-out arrangement at every vertex (“quasi-ice rule”). This constraint alone produces a state, ideal quasi-ice, with an entropy density of 0.724 bits/island. Interaction between (mono)pole-strengths Q at neighboring vertices[21, 22] reduce the ground state degeneracy to 0.15 bits/island by favoring $Q = -1$ (2-in/1-out) next to $Q = +1$. The contrast between the square and honeycomb lattice ground states – two-fold degenerate versus macroscopically degenerate – provides an opportunity to investigate the interplay between the strictures of kinetic constraint and the freedom of massive degeneracy.

We now develop a method to extract the entropy densities on our lattices from the measured configurations of the island magnetic moments. Consider a finite cluster Λ of islands, for example, the 5-island cluster comprising two adjacent vertices (See Fig. 2 legend) and the collection of random variables σ_Λ which are the spins belonging to Λ . The Shannon(-Gibbs-Boltzmann) entropy[23–25] of $P_\Lambda(\sigma_\Lambda)$, the distribution of σ_Λ , is

$$S(P_\Lambda) = - \sum_{\sigma_\Lambda} P(\sigma_\Lambda) \log_2 P(\sigma_\Lambda), \quad (1)$$

where the sum runs over all possible values of the random variable(s) σ_Λ . Note that S is rendered dimensionless by omitting Boltzmann’s constant, and the base of the logarithm is 2, so that the units are bits. If Λ is taken ever larger while the fraction of islands on the edge tends to zero (van Hove limit), we obtain the bulk entropy density s :

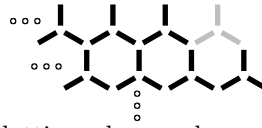
$$s = \lim_{\Lambda \nearrow \infty} \frac{S(P_\Lambda)}{|\Lambda|}. \quad (2)$$

If each island moment independently points either way with probability 1/2, then the entropy density is one bit per island, the largest possible. Lower entropy density indicates correlations in a generic sense. For example, the fully-polarized initial state created by a large H_{ext} has zero entropy density.

The obvious approximation to s suggested by Eq. (2) is simply $S(P_\Lambda)/|\Lambda|$ for the biggest practicable cluster. But this “simple cluster-estimate” is not very good because the configuration space grows exponentially with cluster size $|\Lambda|$, while boundary-crossing correlations are

completely neglected. To understand the latter point, suppose the entire lattice covered without gaps or overlap by translates of Λ . The state constructed from the marginals of P on those translates, *taking them independent*, has entropy density exactly $S(P_\Lambda)/|\Lambda|$. However, short-range boundary-crossing correlations are the same as corresponding intra-cluster correlations, so are reflected in small-cluster data and can be properly counted using *conditional entropy*. The method resembles one proposed some years ago[26, 27] for Monte Carlo simulations of lattice spin models in equilibrium.

One way to think of the total entropy of a given macrostate is as the average uncertainty about the *particular* microstate at hand. Imagine a microstate of the honeycomb lattice revealed three islands (one vertex) at a time, row-by-row. One instant in the process looks like this (the grey vertex is about to be re-

vealed):  Neglecting the (far

distant) lattice edge, each newly revealed vertex bears the same spatial relation to those already known, so the revelation, on average, reduces the uncertainty by exactly 3 times the entropy per spin. Cast this way, the entropy density appears as a *conditional* entropy [28]. The conditional entropy of σ_Λ given σ_Γ is

$$S(\sigma_\Lambda|\sigma_\Gamma) = - \sum_{\sigma_\Lambda, \sigma_\Gamma} P(\sigma_\Lambda, \sigma_\Gamma) \log_2 P(\sigma_\Lambda|\sigma_\Gamma), \quad (3)$$

where $P(\sigma_\Lambda|\sigma_\Gamma) = P(\sigma_\Lambda, \sigma_\Gamma)/P(\sigma_\Gamma)$ is the conditional probability of σ_Λ given σ_Γ . The joint entropy of σ_Λ and σ_Γ then has the pleasant decomposition $S(\sigma_\Lambda, \sigma_\Gamma) = S(\sigma_\Lambda|\sigma_\Gamma) + S(\sigma_\Gamma)$. (Learning σ_Γ and σ_Λ at once is the same as learning σ_Γ and then σ_Λ .) Note that if Λ and Γ overlap, common spins contribute zero to $S(\sigma_\Lambda|\sigma_\Gamma)$.

As a simple illustration, suppose Λ and Γ are single islands, with the probabilities for $P(\sigma_\Lambda, \sigma_\Gamma)$ being given by $P(\downarrow, \uparrow) = 0$ and $P(\uparrow, \uparrow) = P(\uparrow, \downarrow) = P(\downarrow, \downarrow) = 1/3$. If we know that $\sigma_\Gamma = \uparrow$, then the remaining uncertainty about σ_Λ is zero, but if we know that $\sigma_\Gamma = \downarrow$, then the uncertainty is total: 1 bit. Weighting by the probabilities of σ_Γ to be \uparrow or \downarrow gives the entropy of σ_Λ conditioned on σ_Γ : $P(\sigma_\Gamma = \uparrow) \cdot (0) + P(\sigma_\Gamma = \downarrow) \cdot (1) = 2/3$ bit.

The Methods section explains how conditional entropy and other basic notions of information theory can be used to obtain good approximations to the entropy density s from limited data. The result of applying two such approximations to the experimental data for honeycomb lattices are plotted in Fig. 2 as a function of field step size ΔH_{ext} for each lattice constant, along with one simple cluster-estimate for comparison. Data-set sizes are reported in Supplementary Information §1. The simple cluster-estimate $S(\Lambda)/|\Lambda|$ using the five-island di-vertex (Fig. 2 legend) provides a very poor bound compared to our conditioning technique. Reducing lattice constant or

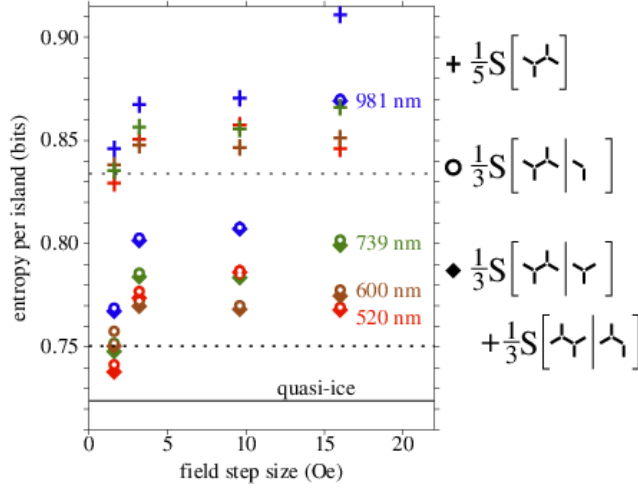


FIG. 2. **Entropy density upper bounds for honeycomb artificial spin ice at four lattice constants as a function of the demagnetization step size ΔH_{ext} .** All bounds are derived using configuration statistics for the 5-island cluster Λ_5 shown in the inset. Crosses are the direct estimate $S(\Lambda_5)/5$, while filled diamonds use inequality (7) and open circles use inequality (5). The dashed lines are the result of our technique applied to ideal quasi-ice (every vertex Type-I with no other restrictions), the upper from the simple cluster-estimate, and the lower two (indistinguishable) from the two conditioning approximations. The simple cluster-estimate applied to a single vertex would give 0.86 bit/island. The solid line at 0.724 shows the actual entropy density of ideal quasi-ice. At the smallest lattice constants and smallest step sizes, subtle signs of longer-ranged monopole correlations appear.

step size should lower the entropy since the first leads to stronger interactions, and the second gives interactions a better chance to be the decisive factor for island flips. The expected lattice constant trend is seen but there is an unexpected plateau with respect to ΔH_{ext} .

It makes sense to compare the experimental states to ideal honeycomb quasi-ice through entropy densities. That of honeycomb quasi-ice is 0.724 bit/island (Supplementary Information §2). But proper comparison requires using the same estimates for both systems. Dashed lines in the plot show the estimates for the model system, the upper for the simple cluster-estimate (compare crosses) and the lower two (indistinguishable) for the conditioning estimates. Hence, the 520 nm array at $\Delta H_{\text{ext}} = 1.6$ Oe has *less* entropy than ideal quasi-ice. This can be explained by correlations between net magnetic charge $Q = \pm 1$ of nearest-neighbor vertices. Ideal quasi-ice has a weak anticorrelation: $\langle Q_i Q_j \rangle \approx -1/9$. In some samples, this correlation reaches -0.25, reflected in a small entropy decrease. Complete sublattice ordering, $\langle Q_i Q_j \rangle = -1$, would reduce the entropy to $s \approx 0.15$ bit/island (Supplementary Information §2). This extra correlation may explain the slightly better performance

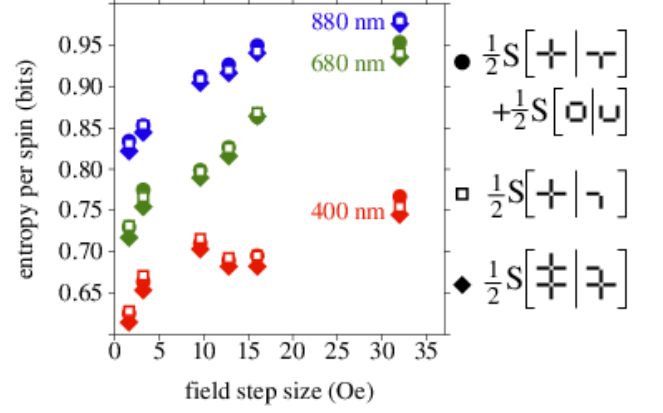


FIG. 3. **Entropy density upper bounds for square lattice artificial spin ice.** The three approximations agree closely. Even extrapolated to zero step size, AC demagnetized square spin ice never approaches the ground state. The diamond estimate is always lower than the square because the former retains more conditioning, whereas the added islands are the same. Dataset sizes are reported in Supplementary Information.

of the bound with a complete vertex in the conditioning data.

The entropy of honeycomb artificial spin ice reveals a state close to ideal quasi-ice, with slight antiferromagnetic vertex charge ordering. The contrasting failure of AC demagnetization of the square lattice to approach the completely ordered ground state is precisely quantified by entropy. We use three approximations (upper bounds) for the square lattice entropy density. They are found by a procedure parallel to that for the honeycomb lattice and are shown in the legend of Fig. 3. The three agree well, and this rough convergence test suggests that they are close to the true entropy densities. As for the honeycomb lattice, we expect smaller entropy for smaller ΔH_{ext} or smaller lattice spacing. In general, this seems to be the case, but the ground state is never approached. Even extrapolations $\Delta H_{\text{ext}} \rightarrow 0$ have large entropy densities.

Closer inspection suggests jamming at ΔH_{ext} . Kinetically constrained approach to ground states defines behavior of complex systems across many fields[19], such as protein folding[14], self-assembly, glasses and granular systems[3–8]. Ergodicity is thwarted by both tall energy barriers and configuration space constrictions, combined into free energy barriers. An ergodic system explores all of configuration space, whereas folding proteins live within a “folding funnel.” This dynamic constriction of allowed configurations introduces many deep conceptual challenges. AC demagnetized artificial spin ice puts the conceptual challenge of kinetic constraint into sharp re-

and

$$2s \leq S \left[\begin{array}{c|c} \begin{array}{c} \text{---} \\ \text{---} \\ \text{---} \end{array} & \begin{array}{c} \text{---} \\ \text{---} \\ \text{---} \end{array} \end{array} \right] \quad (9)$$

and the two-step bound

$$2s \leq S \left[\begin{array}{c|c} \begin{array}{c} \text{---} \\ \text{---} \\ \text{---} \end{array} & \begin{array}{c} \text{---} \\ \text{---} \\ \text{---} \end{array} \end{array} \right] + S \left[\begin{array}{c|c} \begin{array}{c} \text{---} \\ \text{---} \\ \text{---} \end{array} & \begin{array}{c} \text{---} \\ \text{---} \\ \text{---} \end{array} \end{array} \right] \quad (10)$$

A constrained maximum entropy state on the square lattice with given correlations between diagonal and across-the-vertex nearest neighbor correlations coincides with a Gibbs state for an Ising model with effective pair interactions for the two types of nearest neighbors of whatever strength is required to reproduce the required correlations. We have previously [16] studied specific pair correlations in such maximum entropy states using Monte Carlo simulation. Building on the conditioning techniques developed in this Letter, we compute $s(\text{expt}||\text{ME})$, the relative entropy density of an experimental state to the corresponding constrained maximum entropy state. In the case of two probability measures on the configuration space of a lattice system, the relative entropy of their restrictions to some finite region Λ is

$$\begin{aligned} S(Q_\Lambda||P_\Lambda) &= \sum_{\sigma_\Lambda} \log_2 \left(\frac{Q(\sigma_\Lambda)}{P(\sigma_\Lambda)} \right) Q(\sigma_\Lambda) \\ &= \left\langle \log_2 Q_\Lambda \right\rangle_Q - \left\langle \log_2 P_\Lambda \right\rangle_Q. \end{aligned} \quad (11)$$

The limiting relative entropy density which we want is

$$s(Q_\Lambda||P_\Lambda) = \lim_{\Lambda \nearrow \infty} |\Lambda|^{-1} S(Q_\Lambda||P_\Lambda). \quad (12)$$

The logarithm of the probability in Eq. (11) can be expanded in terms of conditionals just as was done for the entropy. For any collection $\{X_1, \dots, X_N\}$ of random variables (the $m = 1$ term being read as an unconditioned probability),

$$\log_2 P(X_N, \dots, X_1) = \sum_{m=1}^N \log_2 P(X_m|X_{m-1}, \dots, X_1)$$

parallels exactly the formula

$$S(X_N, \dots, X_1) = \sum_{m=1}^N S(X_m|X_{m-1}, \dots, X_1).$$

The main difference is that $\log_2 P(\cdot)$ is a random variable, whereas $S(\cdot)$ is a number. Any of the class of approximations for the conditional entropy densities can now be applied to the conditional probabilities to obtain the relative entropy. However, we do not get bounds in this way, just ordinary estimates.

If P_{ME} is a maximum entropy state constrained to have expectations of specified observables match their

expectations in P , then the relative entropy density $s(P||P_{ME})$ ought to equal the difference in the absolute densities. We believe that the method we have used is superior to this simple subtraction because it suppresses the unwanted effects of fluctuations in the counting of low-probability configurations. Due to limited experimental data, configurations which would be expected to have only a few occurrences may have none at all, which has an anomalously large effect in the subtraction. **Acknowledgements.** We acknowledge the financial support from Army Research Office and the National Science Foundation MRSEC program (DMR-0820404) and the National Nanotechnology Infrastructure Network. We are grateful to Prof. Chris Leighton for providing the samples


Author contributions. P.S. and V.H.C. conceived the initial idea of this project, X.K., J.L. and D.M.G. performed the experiments and collected data. C.N. made theoretical contributions. P.E.L. analyzed data and developed theory.

Additional information. Supplementary information accompanies this paper at www.nature.com/naturephysics. Correspondence and requests for materials should be addressed to PEL.


SUPPLEMENTARY INFORMATION 1: DATA SET STATISTICS

All data for each combination of lattice spacing and field step size are gathered after a single demagnetization run, except for 680 nm and 880 nm with $\Delta H_{\text{ext}} = 9.6$ Oe, which incorporate data from two runs. For square lattices, magnetic force microscopy images have size $10\text{ }\mu\text{m} \times 10\text{ }\mu\text{m}$, $17\text{ }\mu\text{m} \times 17\text{ }\mu\text{m}$, or $22\text{ }\mu\text{m} \times 22\text{ }\mu\text{m}$ for lattice constant 400 nm, 680 nm and 880 nm, respectively, in order to have approximately the same number of islands in each image, although this condition is not important to the results. A varying number of images are taken at well-separated points on the array. For honeycomb lattices, a similar procedure was followed. All images are $10\text{ }\mu\text{m} \times 10\text{ }\mu\text{m}$, except for the runs at 1.6 Oe, which, by historical accident, are $6\text{ }\mu\text{m} \times 6\text{ }\mu\text{m}$, $8\text{ }\mu\text{m} \times 8\text{ }\mu\text{m}$, $10\text{ }\mu\text{m} \times 10\text{ }\mu\text{m}$, or $14\text{ }\mu\text{m} \times 14\text{ }\mu\text{m}$ for the 520 nm, 600 nm, 739 nm and 981 nm lattice, respectively.

For honeycomb lattices, from the images, the configu-

ration of every 5-island cluster  or rotation thereof is recorded as a separated data point and all data for a given lattice spacing and ΔH_{ext} is combined. The numbers of such data points entering our analysis are as follows:

Lattice	field step			
	1.6 Oe	3.2 Oe	9.6 Oe	16 Oe
520 nm	831	3332	1754	2836
600 nm	1620	3984	3333	2291
739 nm	1964	2244	2759	1770
981 nm	2096	2098	3286	2317

For square lattices, the 7-island cluster  and rotations thereof are used. The sizes of those data sets are:

Lattice	field step					
	1.6 Oe	3.2 Oe	9.6 Oe	12.8 Oe	16 Oe	32 Oe
400 nm	3861	2729	5523	6363	4158	4699
680 nm	3848	2225	1843	1793	3595	1870
880 nm	3074	3196	3079	3268	3870	3001

The raw data (MFM scans) for square lattice arrays used here were the basis of a previously published study[16].

SUPPLEMENTARY INFORMATION 2: ENTROPIES OF HONEYCOMB LATTICE IDEAL STATES

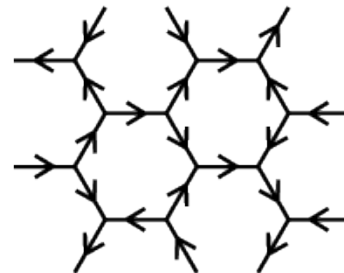
In this section, we substantiate claims in the Letter about the entropies of two ideal states on the honeycomb

lattice: quasi-ice and quasi-ice with full sublattice polarization. The former is the state obtained by imposing the quasi-ice rule (2-in/1-out or 1-in/2-out) at every vertex. The latter is more restricted: vertices on one sublattice must be 2-in/1-out ($Q = -1$) and those on the second sublattice, 1-in/2-out ($Q = +1$). This is a broken symmetry state as it entails a choice of which sublattice is which; for our purposes, we simply pick one.

Quasi-ice

We will show that the quasi-ice state is equivalent to the ordinary nearest-neighbor Ising model having spins at the vertices of the honeycomb lattice, at the special coupling value $\tanh(J/k_B T) = 1/3$. On a given graph with periodic boundary conditions, the partition functions of the two models differ only by a trivial factor: quasi-ice degrees of freedom reside on the edges of the graph, those of the Ising model, on the vertices. Quasi-ice is a combinatorial problem, so the logarithm of the partition function is precisely the entropy we need. The equivalence equates it with the *free energy* of the honeycomb-lattice Ising model at a special temperature, which is available from the exact solution[30–32]. Alternatively, the expansion developed below can be used directly.

The equivalence is established through a representation of the quasi-ice partition function in a high-temperature expansion[33, 34]. Here is a fragment of quasi-ice



taken from a lattice Λ equipped with periodic boundary conditions. We think of Λ as a graph with vertex set $V(\Lambda)$ and edge set $E(\Lambda)$. The partition function, which simply counts configurations allowed by the quasi-ice rule is

$$Z_{\Lambda} = \sum_{\sigma_{\Lambda}} \prod_{i \in V(\Lambda)} \mathcal{I}_i(\sigma). \quad (13)$$

The sum is over *all* assignments of arrows to the edges (as in the figure), and the factors $\mathcal{I}_i(\sigma)$ represent the quasi-ice-rule: $\mathcal{I}_i(\sigma)$ is equal to one if the configuration σ on the edges incident to vertex i satisfy the rule, otherwise it is zero.

To proceed, we introduce extra variables. *Two* “spins” are assigned to the edge ij , σ_i^j , belonging to vertex i

and σ_j^i , belonging to vertex j . We can think of them as arrows, or as ± 1 -valued objects: σ_i^j is regarded to be $+1$ if the corresponding arrow points away from vertex i . Then we remove the redundancy by requiring $\sigma_i^j = -\sigma_j^i$, writing the partition function as

$$Z_\Lambda = \sum_{\{\sigma_i^j\}} \prod_{i \in V(\Lambda)} \mathcal{I}_i(\sigma) \prod_{ij \in E(\Lambda)} \delta(\sigma_i^j, -\sigma_j^i). \quad (14)$$

The point of this maneuver is that the Kronecker deltas can be rewritten as

$$\delta(\sigma_i^j, -\sigma_j^i) = \frac{1 - \sigma_i^j \sigma_j^i}{2}, \quad (15)$$

which form allows expansion. The same trick was used by Nagle[35] for the square lattice ice model. The partition function can thus be written as,

$$Z = 2^{-|E|} Z^{(0)} \left\langle \prod_{ij \in E(\Lambda)} (1 - \sigma_i^j \sigma_j^i) \right\rangle_0, \quad (16)$$

where $\langle \cdot \rangle_0$ denotes expectation in the system of decoupled vertices, which has partition function

$$Z_\Lambda^{(0)} = \sum_{\{\sigma_i^j\}} \prod_{i \in V(\Lambda)} \mathcal{I}_i(\sigma). \quad (17)$$

Since the quasi-ice constraint \mathcal{I}_i allows six configurations of spins attached the vertex i ,

$$Z^{(0)} = 6^{|V|} = (6^{2/3})^{|E|}. \quad (18)$$

The prefactor to the expectation in Eq. (16) is

$$e^{(\frac{2}{3} \log 6 - \log 2)|E|} \quad (19)$$

The coefficient of $|E|$ in the exponent is $0.50136 = 0.7233$ bit. This zero-order approximation to the quasi-ice entropy density is already fairly accurate.

The product in the expectation is now expanded as

$$\prod_{ij \in E} (1 - \sigma_i^j \sigma_j^i) = \sum_{G \subseteq E} \prod_{ij \in G} (-\sigma_i^j \sigma_j^i). \quad (20)$$

The crucial observation at this point is that $\langle \sigma_i^j \rangle_0 = 0$ and $\langle \sigma_i^j \sigma_i^k \sigma_i^l \rangle_0 = 0$ when j, k and l are distinct, because the quasi-ice rule is spin-flip invariant. Also $\langle \sigma_i^j \sigma_i^k \rangle_0 = -1/3$. This shows that when the expectation of the expansion in Eq. (20) is taken, the term for graph G yields zero unless it has an even number (0 or 2) of edges incident on each vertex. Further, G must consist of simple closed loops, no two of which have vertices in common. This follows from the fact that there are only three edges of Λ incident on each vertex. If two belong to G , the third cannot, and the first two must be part of a simple closed loop. For each vertex in a loop, we get a factor $\langle \sigma_i^j \sigma_i^k \rangle_0 = -1/3$,

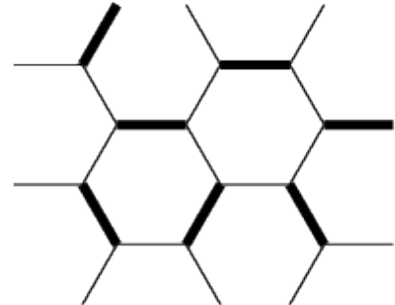
and for each edge, a factor -1 [from Eq. (20)]. Since a closed loop γ has an equal number of edges and vertices, the minus signs cancel and its weight is simply $(1/3)^{|\gamma|}$. Thus,

$$\left\langle \prod_{ij \in E(\Lambda)} (1 - \sigma_i^j \sigma_j^i) \right\rangle_0 = \sum_{\text{disjoint } \{\gamma_\alpha\}} \prod_{\alpha} \left(\frac{1}{3}\right)^{|\gamma_\alpha|}. \quad (21)$$

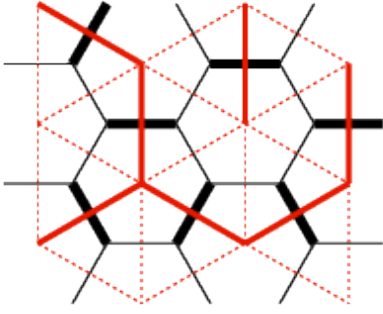
By comparing to the high-temperature expansion of the honeycomb lattice Ising model, $(3^{1/3}/2^{1/2})^{|E|} Z_\Lambda$ is seen to be equal to the Ising model partition function at $\tanh J = 1/3$. From an exact solution for the latter model (references above), $s = 0.724$ bit/island. It is also practical to apply polymer expansion techniques to the right-hand side of Eq. (21).

Vertex-charge-ordered quasi-ice

If the quasi-ice constraint is strengthened to require that all vertices on one sublattice are 2-in/1-out ($Q = -1$) and all on the second sublattice are 1-in/2-out ($Q = +1$), the vertex-charge-ordered quasi-ice state is obtained. We show how to match the configurations of this state one-to-one with those of the triangular lattice Ising antiferromagnet at zero temperature. Since an exact solution[32, 36, 37] is available for the latter, the problem is again solved. The equivalence in this case is a simple observation. Each vertex on the first sublattice has precisely one *out* island, and that island is the only one pointing *in* to the vertex at its other end. Thus, each vertex-charge-ordered quasi-ice configuration corresponds to one *dimer covering* of the lattice: a selection of edges such that each vertex is touched by exactly one. For example,



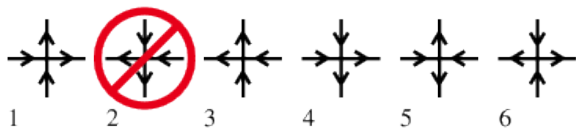
Passing to the dual lattice, which is a triangular lattice, we get a picture like this



in which one edge of each triangle is selected. Now identifying these as the frustrated bonds of an Ising model on the triangular lattice ($\sigma_i \sigma_j = +1$), it is clear that the dimer coverings are in one-to-one correspondence with ground state configurations of the triangular lattice Ising antiferromagnet. Transcribing exact results for that model[32, 36, 37], $s = 0.155$ bit/island.

The vertex-charge-ordered quasi-ice state is also equivalent to a 5-vertex model in which one of the vertices of the usual 6-vertex model is forbidden (see figure below). Wu[38] first noted the equivalence of the honeycomb lattice dimer problem with a 5-vertex model under the name “modified KDP model.” Blöte and Hilhorst[39] noticed the connection with the triangular lattice Ising antiferromagnet. The 5-vertex model is of interest as a model of the terrace-ledge-kink picture of surface growth[40].

We indicate how the connection is made. First, deform the angles in the honeycomb to make a brickwork (ladder) lattice as at the top of Figure 4. Vertices are paired up according to the shaded blocks. Without loss of generality, assume that the sublattice symmetry is broken such that the left-hand vertices in each block are 2-in/1-out and the right-hand ones are 1-in/2-out. It is easy to see that the arrows on the edges inside the blocks are fully determined by the others. So, the blocks may be contracted to vertices on a square lattice as at the bottom, and the vertices can be uniquely re-expanded to reconstruct the original lattice. The vertices which occur (with equal weight) are five of the six vertices of the 6-vertex square ice model[31]; one is forbidden,



because it has two outgoing (ingoing) arrows for the left-hand (right-hand) vertex of a block.

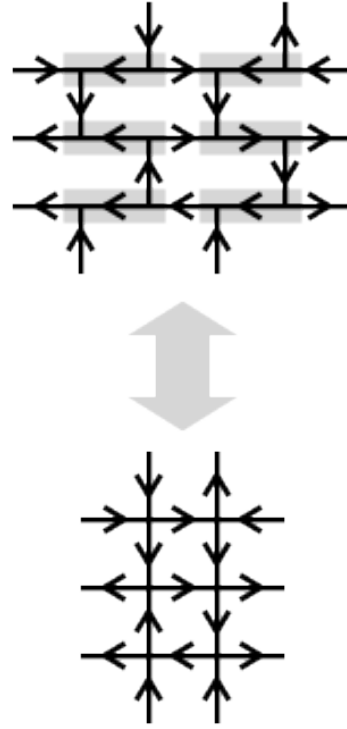


FIG. 4. Equivalence between vertex-charge-ordered quasi-ice and a 5-vertex model.

SUPPLEMENTARY INFORMATION 3: MACROSTATE MIXTURES

Suppose the macrostate produced by the experimental protocol was nonunique, for example, if the array was left with macroscopic magnetization pointing in a random direction, or if the island interactions led to a spontaneous symmetry breaking. Then, sampling over the course of multiple runs would be tantamount to sampling from a mixture of macrostates, corrupting the entropy measurement with a spurious entropy of the mixture. It is interesting to see how much our technique is affected by this problem. Labelling distinct macrostates by θ , assume for simplicity that they all have the same entropy density, as would hold in case of a broken symmetry. Then, what we want is the entropy conditioned on θ . Apropos the straightforward method, observe that $S(\sigma) - S(\sigma_\Lambda|\theta) = S(\theta) - S(\theta|\sigma_\Lambda)$, so that the spurious entropy counted for a cluster is the average information that cluster provides about the macrostate parameter. On the other hand, for the conditioning technique, $S(\sigma_\Lambda|\sigma_\Gamma) - S(\sigma_\Lambda|\sigma_\Gamma, \theta) = S(\theta|\sigma_\Lambda, \sigma_\Gamma) - S(\theta|\sigma_\Gamma)$, so that the spurious entropy count is only the *additional* information about θ brought by σ_Λ , over what is already provided by σ_Γ . In general, this would seem to be another superiority of our technique compared to the straightforward one.

The relation of this to our data analysis has two sides. First, for most combinations of lattice spacing and ΔH_{ext} , our data come from a single run anyway. However, there is ample evidence that there is no overt cooperative symmetry breaking; the only sort of multiple macrostates would be a residual magnetization. We have symmetrized our raw data over discrete lattice symmetries, as a way to reduce sampling error under the assumption that the underlying state respects those symmetries. There are indications that the largest step size (32 Oe) may result in a slight residual macroscopic magnetization, in which case the symmetrization procedure may be questioned. Even supposing the residual magnetization to be present, however, the symmetrization only reduces it by a small discrete symmetry and therefore leaves most of its effects intact.

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